

## Study of irradiated Hadfield steel using transmission Mössbauer spectroscopy with high velocity resolution and conversion electron Mössbauer spectroscopy

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**Abstract.** Proton irradiated Hadfield steel foil was studied using transmission Mössbauer spectroscopy with high velocity resolution and conversion electron Mössbauer spectroscopy. It was shown that proton irradiation leads to structural changes in the foil as well as to surface oxidation with ferric hydrous oxide formation (ferrihydrite). Moreover, oxidation on the foil underside was higher than on the foil right side.

### 1. Introduction

Radiation effects on iron alloys are subject to various studies including Mössbauer spectroscopy [1]. This is very important for analysis of alloys aging and corrosion in nuclear reactors. Mössbauer spectroscopy is useful for analysis of structural damages and oxidation processes in irradiated alloys. Therefore in the present work we discuss results of the study of the effect of proton irradiation in Hadfield steel foil by Mössbauer spectroscopy using transmission and conversion electrons techniques.

### 2. Materials and methods

Hadfield steel (19 wt% Mn, 0.8 wt% C and Fe as a balance) foil with thickness of 20  $\mu\text{m}$  (rolling with high temperature annealing) was irradiated with protons (energy of 5.7 MeV, fluence of  $5 \times 10^{15}$  particles/cm<sup>2</sup>). Non-irradiated and irradiated foils were studied at room temperature using transmission Mössbauer spectroscopy with high velocity resolution and conversion electron Mössbauer spectroscopy (CEMS) with back scattering counter with He using high precision and sensitive spectrometer SM-2201.

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Characteristics of Mössbauer spectrometer SM-2201 with high velocity resolution were described in details in [2]. Spectra were measured in 4096 channels and then presented in 1024 channels for transmission spectra and in 512 channels for CEMS spectra. Mössbauer spectra were computer fitted with the least squares procedure using UNIVEM-MS program with Lorentzian line shape. Mössbauer parameters isomer shift  $\delta$ , quadrupole splitting (quadrupole shift for magnetically split component)  $\Delta E_Q$ , magnetic hyperfine field  $H_{\text{eff}}$ , line width  $\Gamma$ , subspectrum relative area  $S$  and statistical criterion  $\chi^2$  were determined. Magnetic sextets were fitted using the ratio  $S_{16}:S_{25}:S_{34}=3:2:1$  for transmission spectra and equal  $S_{16}:S_{25}:S_{34}$  ratio for sextets in CEMS spectra. The values of isomer shift are given relative to  $\alpha$ -Fe at 295 K.

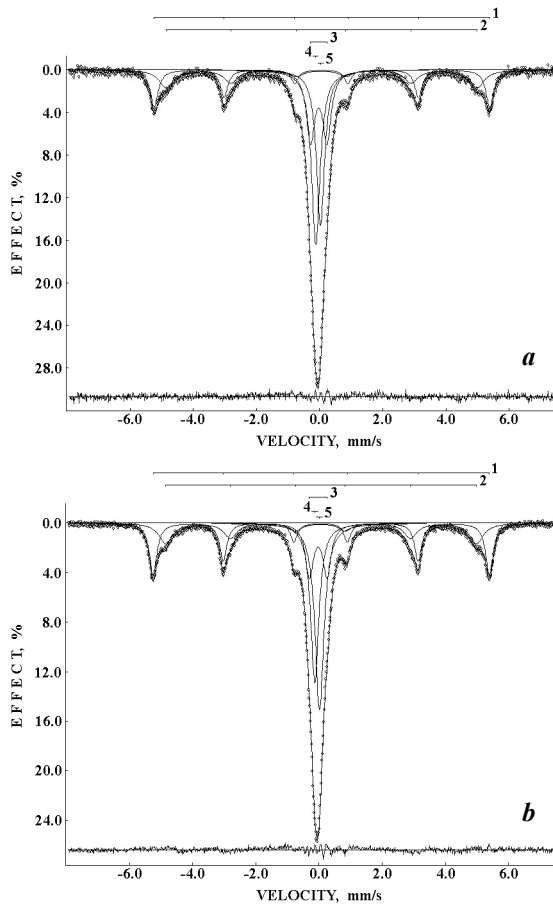
### 3. Results and Discussion

Mössbauer spectra of irradiated foil obtained using transmission spectroscopy with high velocity resolution and CEMS are shown in Figures 1 and 2. Transmission spectra of non-irradiated and irradiated foil were better fitted using two sextets (1 and 2), one doublet (3) and two singlets (4 and 5). Mössbauer hyperfine parameters for these components were similar for non-irradiated and irradiated foils and related to iron environment correspondent to  $\alpha$ -Fe ( $H_{\text{eff}}$  were  $329.9 \pm 0.5$  and  $330.7 \pm 0.5$  kOe, respectively), Fe-Mn ( $H_{\text{eff}}$  were  $305.7 \pm 0.5$  and  $305.6 \pm 0.5$  kOe, respectively), Fe-C ( $\Delta E_Q$  and  $\delta$  were  $0.521 \pm 0.015$  mm/s,  $-0.025 \pm 0.015$  mm/s and  $0.558 \pm 0.015$  mm/s,  $-0.024 \pm 0.015$  mm/s, respectively),  $\epsilon$ -Fe ( $\delta$  were  $-0.120 \pm 0.015$  and  $-0.132 \pm 0.015$  mm/s, respectively) and  $\gamma$ -Fe ( $\delta$  were  $0.029 \pm 0.015$  and  $0.017 \pm 0.015$  mm/s, respectively). Therefore, these components and iron environments were further denoted as  $\alpha$ -Fe, Fe-Mn, Fe-C,  $\epsilon$ -Fe and  $\gamma$ -Fe, respectively. However, relative areas of these components were changed after irradiation (Figure 3). Relative area of  $\alpha$ -Fe component increased from  $\sim 19$  to  $\sim 24$  %, while that of Fe-C component decreased from  $\sim 19$  to  $\sim 13$  % as well as relative area of  $\epsilon$ -Fe decreased from  $\sim 25$  to  $\sim 20$  % while that of  $\gamma$ -Fe component increased from  $\sim 21$  to  $\sim 25$  %. Relative area of Fe-Mn component remained the same. These results demonstrated that proton irradiation of the foil led to removing of C from iron environment and, therefore, increasing of  $\alpha$ -Fe environment as well as transformation of  $\epsilon$ -Fe environment into  $\gamma$ -Fe one.

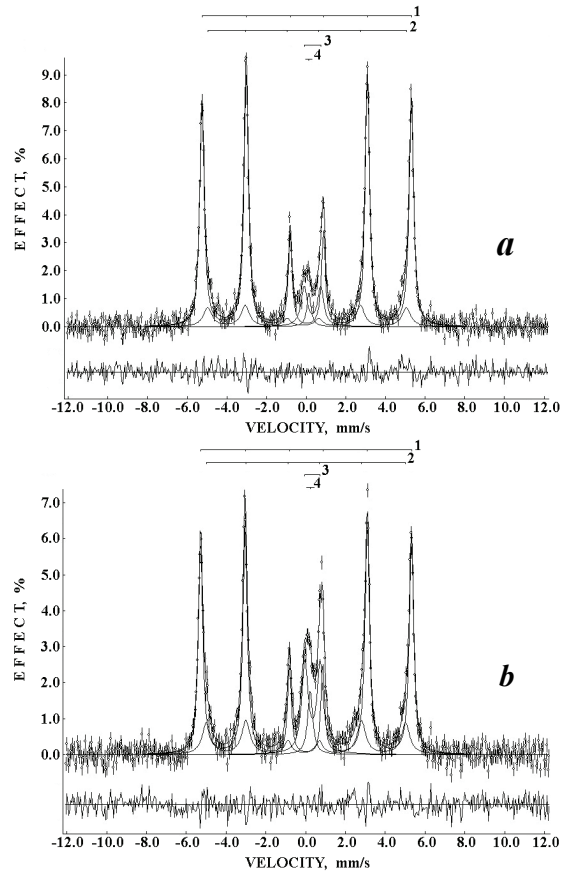
The results of the fitting of conversion electron Mössbauer spectra showed that non-irradiated foil spectrum consisted of three components which may be related to  $\alpha$ -Fe ( $H_{\text{eff}}$  value was  $328 \pm 1$  kOe), Fe-Mn ( $H_{\text{eff}}$  value was  $315 \pm 1$  kOe) and  $\epsilon$ -Fe ( $\delta$  value was  $-0.05 \pm 0.05$  mm/s). Spectra of the right side and underside of irradiated foil consisted of two sextets which were related to  $\alpha$ -Fe ( $H_{\text{eff}}$  values were  $328 \pm 1$  kOe and  $329 \pm 1$  kOe) and to Fe-Mn ( $H_{\text{eff}}$  values were  $311 \pm 1$  kOe and  $311 \pm 1$  kOe), one quadrupole doublet with parameters  $\delta = 0.31 \pm 0.05$  mm/s,  $\Delta E_Q = 0.83 \pm 0.05$  mm/s and  $\delta = 0.35 \pm 0.05$  mm/s,  $\Delta E_Q = 0.77 \pm 0.05$  mm/s, and one singlet which was related to  $\gamma$ -Fe ( $\delta$  values were  $0.14 \pm 0.05$  mm/s and  $0.23 \pm 0.05$  mm/s). Parameters of revealed doublet were similar to ferric hydrous oxides such as akaganite ( $\beta$ -FeOOH) or ferrihydrite (see data for comparison in [3]).  $\beta$ -FeOOH was considered as a corrosion product of steel corrosion including corrosion in the nuclear reactor [4]. However, we can consider ferrihydrite as a result of foil oxidation in the absence of  $\text{Cl}^-$  ions. It was interesting to observe twice increase of relative area of ferrihydrite component in the spectrum of the underside of irradiated foil (Figure 4). It is possible that energy lost with protons passing foil raises protons interaction cross-section with indoor air molecules ( $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ) with formation of radicals, ozone, oxygen atoms, etc. Therefore, radiation induced corrosion in the foil increases with increase of products of radiolysis in the air.

### 4. Conclusion

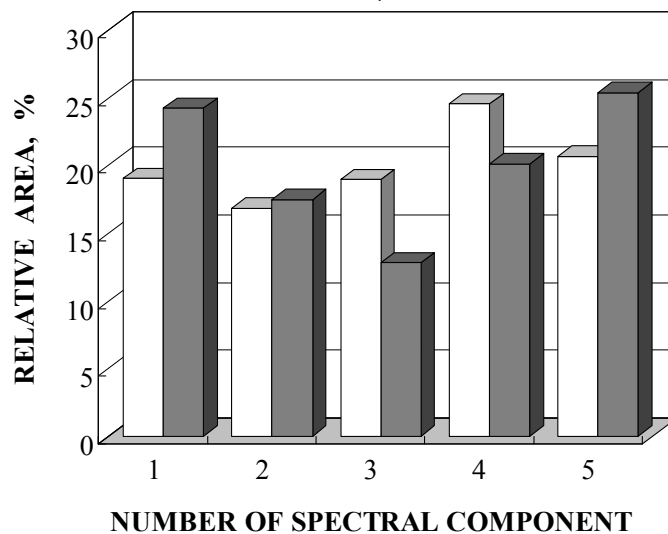
Comparative study of the Hadfield steel foil non-irradiated and irradiated with protons using Mössbauer spectroscopy demonstrated structural variations in the foil after irradiation as well as surface oxidation with ferrihydrite formation. It was also shown that radiation induced oxidation was higher on the underside of the foil.



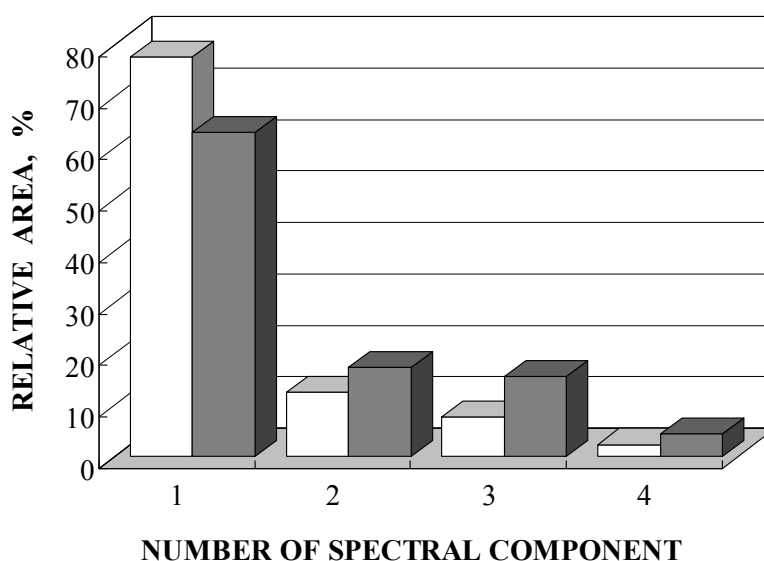
**Figure 1.** Transmission Mössbauer spectra of Hadfield steel foils presented in 1024 channels: non-irradiated (*a*) and irradiated with protons (*b*). 1 –  $\alpha$ -Fe, 2 – Fe-Mn, 3 – Fe-C, 4 –  $\epsilon$ -Fe, 5 –  $\gamma$ -Fe. T=295 K.



**Figure 2.** Conversion electron Mössbauer spectra of Hadfield steel foil irradiated with protons presented in 512 channels: the right side of the foil (*a*) and the underside of the foil (*b*). 1 –  $\alpha$ -Fe, 2 – Fe-Mn, 3 – ferrihydrite, 4 –  $\gamma$ -Fe. T=295 K.



**Figure 3.** Relative areas of spectral components for transmission Mössbauer spectra of Hadfield steel foils: non-irradiated (white) and irradiated with protons (grey). 1 –  $\alpha$ -Fe; 2 – Fe-Mn; 3 – Fe-C; 4 –  $\epsilon$ -Fe; 5 –  $\gamma$ -Fe. Error for relative areas was 10 % or less.



**Figure 4.** Relative areas of spectral components for conversion electron Mössbauer spectra of Hadfield steel foil irradiated with protons: the right side of the foil (white) and the underside of the foil (grey). 1 –  $\alpha$ -Fe, 2 – Fe-Mn, 3 – ferrihydrite, 4 –  $\gamma$ -Fe. Error for relative areas was 10 % or less.

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